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Novel Polyarylene−Triarylmethane Dye Copolymers

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ABSTRACT: In this work, we discuss a useful and proper way to get new triarylmethane dyes carrying two bromine functionalities offering the possibility for polycondensation via the Suzuki cross-coupling reaction. The molecular weights of the new copolymers **P1-OH**−**P4-OH** are determined for the leuco forms by GPC (polystyrene standard). Conversion of the leuco form to the colored form is done in dichloromethane with trifluoroacetic acid.

Introduction

During the past two decades, conjugated polymers have come to the focus of investigation.[1] Because of their electrical conductivity and semiconductivity, they offer a wide range of applications. Exemples for use include polymer batteries,[2] transistors,[3] organic light-emitting diodes (OLEDs),[4] and most importantly, polymer-based solar cells.[5]

To become a useful and economic alternative to silicon-based solar cells, it will be necessary to maximize the efficiency of these organic solar cells. One facet in the complex field of tuning the optoelectrical properties is the adjustment of the absorption maximum (λ_{max}) of polymers. It is clear, that the absorption maxima should be placed near or in the range of the maximum solar emission that lies between 550 and 750 nm.[6]

Well-known polymers such as poly-[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) or analogue substituted PPVs absorb at about 450−500 nm.[7] According to the literature, there are many more polymers and oligomers of the poly(*p*-phenylene ethynylene) group (PPE) with an absorption maximum at about 430−480 nm.[8] Furthermore, papers have been published about polymers that contain comonomers such as anthracene, benzothiadiazole, thiophene, or the like to tune the optical properties.[9] Polymers containing metal centers (e.g., ruthenium) as chromophores are used[10] to shift λ_{max} bathochrome.

To the best of our knowledge, only one polymer containing a dye as chromophoric group, covalently integrated in the backbone of a conjugated polymer,[11] has been described in the literature so far.

This article describes the synthesis of four new polyarylene copolymers containing triarylmethane dyes in the leuco and the salt forms as components of the main chain.

As it is known, the group of triphenylmethane dyes (TPMD) offers a wide range of substances with absorption maxima between 450 and 650 nm (ϵ = 30 000−100 000 L mol^{-1} cm^{-1}). In the case of the colored form, the dyes are very strong electron acceptors.

Experimental Section

General. *Materials.* All starting materials were purchased from commercial suppliers such as Merck, Aldrich, Lancaster, or Fluka. Toluene, benzene, and tetrahydrofuran (THF) were predried over KOH and, if not otherwise specified, distilled over sodium/benzophenone. Prior to all Suzuki cross-coupling reactions, the toluene/water mixtures were degassed by sparkling for 2 h with argon. The monomers phenylenediboronic acid-bis-pinacolester (**2a**),[12] 2,7-(diboronic-bis-ethyleneglycolester)-9,9′-dioctylfluorene (**2c**),[13] 2,7-dibromo-9,9′-dioctylfluorene (**3a**),[14] 1,4-dibutoxy-2,5-diiodbenzene (**3c**),[15] 3,4-dihexylthiophene, and 3,4-dihexyl-2,5-dibromthiophene (**3b**)[16] were synthesized in accordance with the literature.

Methods. ^{1}H NMR and ^{13}C NMR spectra were obtained in deuterated solvents using a Bruker AC 250 and DRX 400, respectively. Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Elemental analysis was performed with a CHNS-932 Automat Leco. A homemade electromagnetic compensated thermoscale with an optoelectronic measurement served for the thermogravimetry. Gel permeation chromatography (GPC) was performed on a set of apparatuses of Knaur using THF as eluent and polystyrene as the standard. The UV−vis absorption spectra were recorded in highly diluted solutions ($\approx 10^{-5}$ M) on a Perkin-Elmer UV/Vis-NIR spectrometer Lambda 19.

Synthesis of Monomers. *4,4′-Dibromo-(4″-N,N-dimethylamino)triphenylmethanol (**1a**).* A solution of *n*-butyllithium (1.6 M in hexane, 2.7 mL, 4.3 mmol) in THF (30 mL) was cooled to −78 °C. Within 30 min, a solution of 4-bromo-*N*,*N*-dimethylaniline (0.8 g, 4.1 mmol) in 50 mL THF was added dropwise. A white precipitate occurred. The mixture is stirred for another 2 h. This mixture was dropped through a double cannula into a solution of 4,4′-dibromobenzophenone (1.4 g, 4.1 mmol) in 50 mL of THF cooled to −78 °C. The dropping rate was controlled by the argon pressure and was set at about two drops per second. After complete addition, the mixture was allowed to reach room temperature and was stirred for additional 2 h. Then a saturated aquatic solution of NH_4Cl was added, the mixed phases were extracted five times with chloroform, the combined organic phases were washed with water twice, and then dried over magnesium sulfate. Chromatography on SiO_2 with hexane/ethyl acetate 5:1 yields white coarse crystals; yield: 1.4 g (73%). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 2.62 (s, 1H, O*H*), 2.86 (s, 6H, N−*Me*$_2$), 6.55, 6.92 (AA′XX′, 4H, aniline), 7.09, 7.33 (AA′XX′, 8H). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 40.4 (N−*Me*$_2$), 81.2 (*C*−OH), 111.8, 121.3, 127.9, 128.7, 129.6, 130.9, 133.7, 146.0, 149.9. Anal. Calcd for $C_{21}H_{19}OBr_2N$ (461.2): C, 54.69; H, 4.15; N, 3.04; Br, 34.65. Found: C, 54.82; H, 4.24; N, 2.92; Br, 34.88.

2,5-Dibromobenzophenone. A two-necked flask was charged with 2,5-dibromobenzoic acid (2.7 g, 9.8 mmol) and 50 mL of thionyl chloride. The suspension was stirred for 1.5 h at 80 °C. Excessive thionyl chloride was removed under reduced pressure at 50 °C, and 50 mL of benzene were added. To start the Friedel−Crafts acylation, $AlCl_3$ (2.6 g, 19.5 mmol) was added and the mixture was stirred under reflux for another 3 h, followed by quenching by pouring it into 100 mL of ice water. The organic layer was washed twice with water, and the combined aquatic phases were extracted

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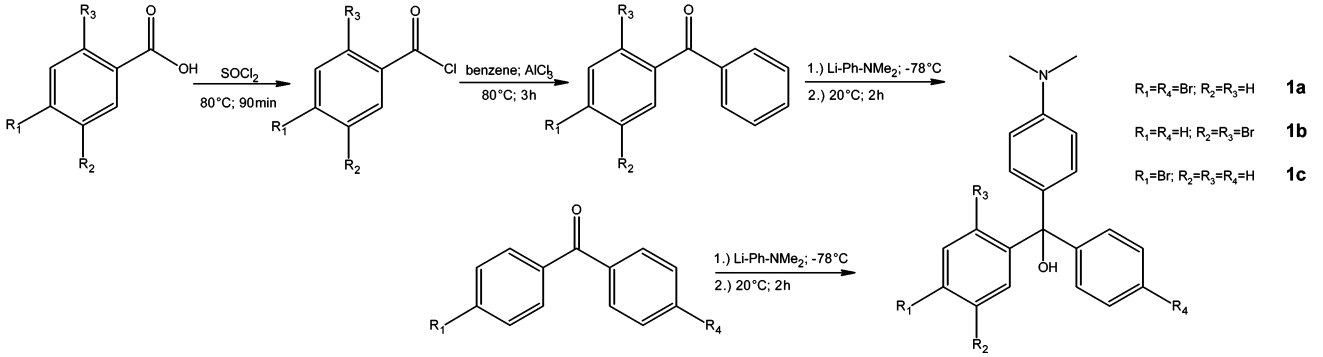
Scheme 1. Synthesis of Triphenylmethane Dye Carbinols (TPM-OH)



three times with chloroform. The combined organic layers were dried over magnesium sulfate, and the solvents were removed under reduced pressure. Column chromatography on SiO_2 with hexane/ethyl acetate 3:1 as eluent and recrystallization from hexane yielded colorless needles; yield: 1.7 g (51%); mp 107 °C. ^1H NMR (250 MHz, $CDCl_3$, δ): 7.46−7.82 (m, 8H). ^{13}C NMR (62 MHz, $CDCl_3$, δ): 118.2, 121.3, 128.8, 130.2, 131.6, 134.0 (2 signals), 134.1 (2 signals), 134.6, 135.5, 142.4, 194.1 ($C{=}O$). Anal. Calcd for $C_{13}H_8OBr_2$ (340.0): C, 45.92; H, 2.44; Br, 47.00. Found: C, 46.09; H, 2.44; Br, 46.77.

*2,5-Dibromo-(4′-N,N-dimethylamino)triphenylmethanol (**1b**).* The synthesis was done similarly to **1a** except for the use of 2,5-dibromobenzophenone (2.4 g, 7.06 mmol) as carbonyl agent. 4-Bromo-*N*,*N*-dimethylaniline (1.5 g, 7.5 mmol); *n*-butyllithium (2.5 M in hexane, 3.0 mL); yield: 1.1 g (34%). ^1H NMR (250 MHz, $CDCl_3$, δ): 2.82 (6H, s, N−*Me*$_2$), 4.18 (1H, s, OH), 6.58, 6.96 (4H, AA′XX′), 7.13−7.36 (8H, m). ^{13}C NMR (62 MHz; $CDCl_3$, δ): 39.5 (N−*Me*$_2$), 81.4 (*C*−OH), 110.8, 120.1, 120.8, 126.3, 126.6, 126.8, 127.2, 130.9, 131.4, 133.1, 135.1, 144.4, 146.8, 148.7. Anal. Calcd for $C_{21}H_{19}Br_2NO$ (461.2): C, 54.69; H, 4.15; N, 3.03; Br, 34.65. Found: C, 55.04; H, 4.39; N, 2.75; Br, 34.21.

Synthesis of Polymers. *General Procedure.*[17] The specific monomers **1**(**a**,**b**)/phenylenediboronic acid-bis-pinacolester **2a**/**3a**−**c** in the ratio of 1:2:1 and 4.5 mol equiv of Na_2CO_3 compared to **2a** were dissolved in a mixture of toluene/water 1:1 v/v (200 mL per 1 g of **1**). Aliquat 336 (phase transfer catalyst) (3 drops per 1 g of **1**) and tetrakis(triphenylphosphine)palladium(0) (2 mol % compared to boronic acid functionalities) were added, and the solution was heated to 100 °C and stirred for 96 h at that temperature. After cooling to room temperature, the phases were separated and the organic layer was washed five times with water. The combined aquatic phases were extracted twice with chloroform, and the combined organic phases were filtered through phase separating paper. The volume of the solution was reduced to a small amount (10−20 mL), and the polymer was precipitated from methanol. The polymer was redissolved in approximately 20 mL of dichloromethane and precipitated from hexane. The procedure was repeated for diethyl ether and methanol.

*Poly-co-[(1,4-phenyl)−(2,7-(9,9′-dioctyl)fluorenyl)]-[(1,4-phenyl)−(4,4′-(4′′-N,N-dimethylamino) triphenylmethanoyl)] (**P1-OH**)* was prepared according to the general procedure. **1a** (1.015 g, 2.2 mmol), **2a** (1.452 g, 4.4 mmol), **3a** (1.207 g, 2.2 mmol), Na_2CO_3 (2.0 g; 19.0 mmol), $Pd(PPh_3)_4$ (0.2 g, 2mol %); yield: 1.5 g (90%). ^1H NMR (250 MHz, CD_2Cl_2, δ) 0.69−1.01 (30H, m), 1.98 (4H, s), 2.75 (1H, s, OH), 2.88 (6H, s), 6.61 (2H, m, *AA′*XX′), 7.10−7.71 (24H, m). ^{13}C NMR (62 MHz, CD_2Cl_2, δ): 13.0, 21.6, 22.8, 28.2, 29.1, 30.8, 39.4, 54.3, 80.6, 110.8, 119.1, 120.4, 124.9, 125.4, 126.0, 126.5, 127.4, 127.9, 130.9, 133.7, 138.5, 139.1, 139.5, 145.5, 148.7, 150.8. Anal. Calcd for $(C_{62}H_{67}NO)_n$ $(842.2)_n$: C, 88.42; H, 8.02; N, 1.66. Found: C, 83.13; H, 7.54; N, 1.02; Br, 0.66. GPC: M_w = 12 000 g/mol, M_n = 7000 g/mol, D = 1.68, DP = 8. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 229 (26 500), 275 (23 000), 300 (25 000), 352 (33 500). The polymer was stable up to 230 °C. No exotherm or endotherm phase transitions could be obtained.

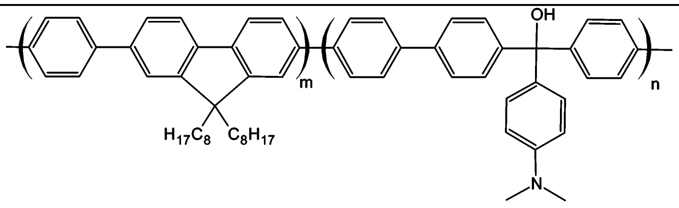
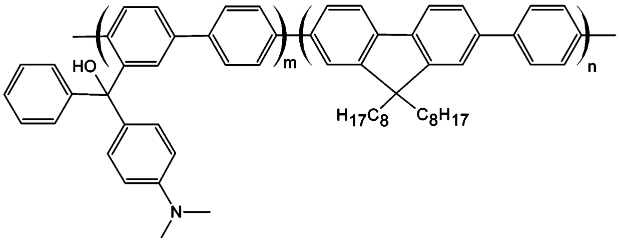
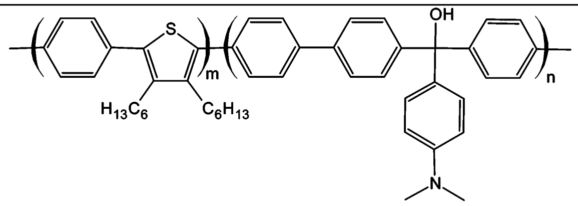
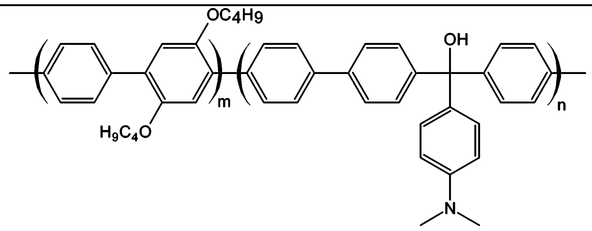
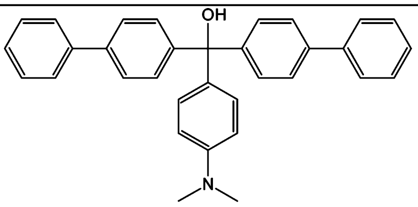
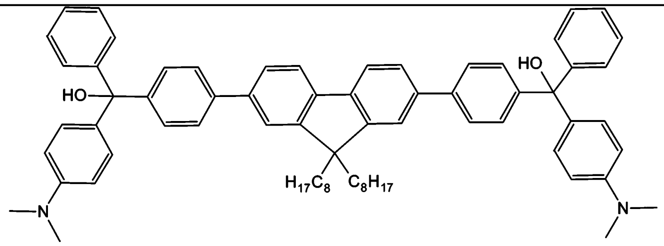
*Poly-co-[(1,4-phenyl)−(2,7-(9,9′-dioctyl)fluorenyl)]-[(1,4-phenyl)−(2,5-(4′-N,N-dimethylamino) triphenylmethanoyl)] (**P2-OH**)* was prepared according to general procedure. **1b** (1.015 g, 2.2 mmol), **2a** (1.452 g, 4.4 mmol), **3a** (1.207 g, 2.2 mmol), Na_2CO_3 (2.0 g, 19.0 mmol), $Pd(PPh_3)_4$ (0.2 g, 2mol %); yield: 1.3 g (71%). ^1H NMR (250 MHz, CD_2Cl_2, δ): 0.85−2.16 (34H, m, b), 3.00 (7H, s, b), 6.73−7.86 (26H, m). ^{13}C NMR (62 MHz, CD_2Cl_2, δ): 14.3, 23.0, 24.3, 29.6, 30.4, 32.2, 40.7, 55.8, 83.8, 112.1, 120.5, 121.8, 125.4, 126.3, 126.9, 127.7, 127.8, 128.1, 128.5, 129.2, 130.4, 133.4, 135.8, 139.9, 140.6, 141.6, 146.8 148.7, 150.2, 152.3. Anal. Calcd for $(C_{62}H_{67}NO)_n$ $(842.2)_n$: C, 88.42; H, 8.02; N, 1.66. Found: C, 87.69; H, 7.92; N, 1.24; Br, 0.70. GPC: M_w = 27 200 g/mol, M_n = 13 500 g/mol, D = 2.02, DP = 16. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 231 (39 000), 270 (27 500), 356 (57 500). The polymer was stable up to 230 °C. No exotherm or endotherm phase transitions could be obtained.

*Poly-co-[(1,4-phenyl)−(2,5-(3,4-dihexyl)thiophenyl)]-[(1,4-phenyl)−(4,4′-(4′′-N,N-dimethylamino) triphenylmethanoyl)] (**P3-OH**)* was prepared according to the general procedure. **1a** (1.015 g, 2.2 mmol), **2a** (1.452 g, 4.4 mmol), **3b** (0.903 g, 2.2 mmol), Na_2CO_3 (2.0 g, 19.0 mmol), $Pd(PPh_3)_4$ (0.2 g, 2 mol %); yield: 0.8 g (54%). ^1H NMR (250 MHz; CD_2Cl_2, δ): 0.87−1.57 (22H, m, b), 2.71 (4H, s), 2.94 (7H, s), 6.68−7.68 (20H, m). ^{13}C NMR (62 MHz; CD_2Cl_2, δ): 13.8, 22.6, 27.7, 29.5, 30.9, 31.4, 40.2, 81.4, 111.7, 126.3, 127.0, 128.3, 128.8, 129.3, 130.8, 134.2, 136.9, 139.4, 146.8, 149.9. Anal. Calcd for $(C_{49}H_{53}NOS)_n$ $(703.9)_n$: C, 83.56; H, 7.59; N, 1.99; S, 4.55. Found: C, 78.05; H, 6.70; N, 1.71; S, 4.82; Br, 5.39. GPC: M_w = 16 000 g/mol, M_n = 10 000 g/mol, D = 1.57, DP = 14. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 230 (103 400), 271 (58 300). The polymer was stable up to 230 °C. No exotherm or endotherm phase transitions could be obtained.

*Poly-co-[(1,4-phenyl)−(1,4-(2,5-dibutoxy)phenyl)]-[(1,4-phenyl)−(4,4′-(4′′-N,N-dimethylamino) triphenylmethanoyl)] (**P4-OH**)* was prepared according to the general procedure. **1a** (1.015 g, 2.2 mmol), **2a** (1.452 g, 4.4 mmol), **3c** (1.043 g, 2.2 mmol), Na_2CO_3 (2.0 g, 19.0 mmol), $Pd(PPh_3)_4$ (0.2 g, 2 mol %); yield: 0.67 g (44%). ^1H NMR (250 MHz, CD_2Cl_2, δ): 0.84 (6H, s), 1.37 (4H, s), 1.64 (4H, s), 2.85 (7H, s), 3.91 (4H, s), 6.60−7.68 (22H, m). ^{13}C NMR (62 MHz; CD_2Cl_2, δ): 14.0, 19.7, 31.9, 40.6, 69.6, 81.8, 112.1, 116.3, 126.7, 126.9, 128.3, 129.1, 129.5, 129.9, 130.7, 131.2, 135.0, 137.5, 139.7, 147.1, 150.3, 150.7. Anal Calcd for $(C_{47}H_{47}NO_3)_n$ $(673.9)_n$: C, 84.02; H, 6.75; N, 2.09. Found: C, 80.78; H, 7.03; N, 1.73; Br, 2.28. GPC: M_w = 6500 g/mol, M_n = 4100 g/mol, D = 1.58, DP = 6. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): = 230 (51 000), 290 (65 000), 343 (42 000). The polymer was stable up to 230 °C. No exotherm or endotherm phase transitions could be obtained.

Synthesis of Model Substances. *(4,4′-Diphenyl)−(4′′-N,N-dimethylamino)-triphenylmethanol (**M1-OH**).* A solution of **1a** (1.0 g; 2.1 mmol), phenylboronic acid ethylene glycol ester **2b** (0.6 g, 2.1 mmol), Na_2CO_3 (0.7 g, 6.4 mmol), $Pd(PPh_3)_4$ (0.1 g, 2 mol %), and Aliquat 336 (3 drops) was heated to 100 °C and stirred at that temperature for 12 h. After cooling to room temperature, the phases were separated and the organic phase was washed five times with water. The aquatic phase was extracted with dichloromethane twice, and the combined organic layers were dried over $MgSO_4$. Column chromatography (SiO_2, hexane/ethyl acetate 5:1) and recrystallization from hexane/ethyl acetate 5:1 yielded a white

Table 1. Overview over Designed Polymers and Model Substances

polymer /model	structure	yield	TPM-OH	ar	λ_{max} [nm] $\epsilon \times 10^3$ [l mol^{-1} cm^{-1}]
P1-OH		90%	**1a**	**3a**	275 300 352 *23 25 36*
P2-OH		71%	**1b**	**3a**	270 356 *27 57*
P3-OH		54%	**1a**	**3a**	271 302 *58 42*
P4-OH		44%	**1a**	**3c**	290 343 *67 42*
M1-OH		55%	**1a**	-	264 *58*
M2-OH		33%	**1c**	-	268 333 *58 76*

powder; yield: 0.5 g (55%). ^{1}H NMR (250 MHz; CDCl$_3$, δ): 2.80 (s, 1H, O*H*), 2.98 (s, 6H, N$-$*Me$_2$*), 6.71, 7.19 (AA′XX′, 4H, aniline), 7.35$-$7.63 (18H, m). ^{13}C NMR (62 MHz, CDCl$_3$, δ): 40.5 (N$-$*Me$_2$*), 81.6 (*C*$-$OH), 111.8, 126.5, 127.0, 121.3, 128.7, 129.0, 134.8, 139.8, 140.8, 146.4, 149.7. Anal. Calcd for $C_{33}H_{29}ON$ (455.6): C, 87.00; H, 6.42; N, 3.07. Found: C, 85.80; H, 6.56; N, 2.74. UV$-$vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 264 (55 500).

4-Bromobenzophenone. Synthesis according to 2,5-dibromobenzophenone. 4-Bromobenzoic acid (4.3 g, 21.6 mmol), thionyl chloride (45 mL), benzene (32 mL), and AlCl$_3$ (4.2 g, 31.5 mmol); yield: 3.9 g (69%). ^{1}H NMR (250 MHz, CDCl$_3$, δ): 7.26$-$7.79 (13H, m). ^{13}C NMR (62 MHz, CDCl$_3$, δ): 127.5, 128.4, 129.9, 131.5, 131.6, 132.6, 136.3, 137.2, 195.6 (C=O). Anal. Calcd for $C_{13}H_9O$ (261.1): C, 59.80; H, 3.47; Br, 30.60. Found: C, 59.61; H, 3.34; Br, 29.09.

*4-Bromo-(4′-N,N-dimethylamino)-triphenylmethanol (**1c**).* Synthesis according to **1a**: 4-bromo-*N*,*N*-dimethylaniline (1.5 g, 7.5 mmol), *n*-butyllithium (3.0 mL, 2.5 M in hexane, 7.5 mmol), 4-bromobenzophenone (1.1 g, 4.0 mmol); yield: 1.2 g (77%). ^{1}H NMR (250 MHz; CDCl$_3$, δ): 2.77 (6H, s, N−*Me$_2$*), 3.04 (1H, s, OH), 6.49, 6.90 (4H, AA′XX′, aniline), 7.03−7.26 (9H, m). ^{13}C NMR (62 MHz, CDCl$_3$, δ): 40.6 (N−*Me$_2$*), 81.5 (*C*−OH), 111.9, 121.1, 127.2, 127.9, 128.0, 129.0, 129.8, 130.9, 134.5, 146.6, 147.0, 149.8. Anal. Calcd for $C_{21}H_{20}NOBr$ (382.3): C, 65.98; H, 5.27; N, 3.66; Br, 20.90. Found: C, 65.99; H, 5.49; N, 3.39; Br, 19.97.

*2,7-Bis-[4-(N,N-dimethylamino)triphenylmethanol-4′-yl]-9,9′-dioctylfluorene (**M2-OH**).* Synthesis according to **M1**: **2c** (0.4 g, 0.8 mmol), **1c** (0.6 g, 1.6 mmol), Pd(PPh$_3$)$_4$ (18 mg; 2 mol %), Na$_2$CO$_3$ (0.4 g; 3.8 mmol); yield: 0.3 g (33%). ^{1}H NMR (400 MHz; CD$_2$Cl$_2$, δ): 0.75 (4H, s(b)), 0.81 (6H, t, $J = 8$ Hz), 0.96−1.10 (20H, m), 2.10 (4H, m), 2.89 (2H, s, OH), 2.98 (12H, s, NMe$_2$), 6.72, 7.17 (8H, AA′XX′, aniline), 7.32−7.85 (24H, m). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, δ): 13.8, 22.6, 23.9, 29.2, 30.0, 31.8, 40.3 (N−*Me$_2$*), 55.3, 81.5 (*C*−OH), 111.7, 120.0, 121.5, 125.9, 126.4, 127.0, 127.8, 128.1, 128.2, 128.8, 134.8, 140.0, 140.1, 146.6, 147.6, 149.9, 151.8. Anal. Calcd for $C_{71}H_{80}N_2O_2$ (993.4): C, 85.84; H, 8.12; N, 2.82. Found: C, 84.85; H, 8.08; N, 2.68; Br, 0.66. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 230 (78 000), 268 (71 000), 334 (108 000).

Conversion of Carbinoles to the Colored Form. *General Procedure.*[18] The particular substance (polymer/model) was dissolved in dichloromethane, and trifluoroacidic acid was added in about a 6-fold molar amount (compared to polymer/model). The colorless solution turned deep violet within minutes. From this solution, NMR spectroscopy, and precipitation is possible.

P1: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 0.67−0.98 (30H, m), 2.01 (4H, s), 3.41 (6H, s), 6.99−7.82 (26H, m). ^{13}C NMR (62 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 14.0, 22.9, 24.3, 29.5, 30.3, 32.1, 42.5, 55.8, 121.2, 121.8, 126.3, 126.5, 127.8, 128.1, 128.2, 128.5, 129.0, 130.3, 132.8, 136.2, 137.8, 138.0, 139.5, 139.9, 140.6, 141.0, 142.1, 144.0, 144.2, 147.5, 148.3, 152.3, 178.5. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 354 (50 500), 537 (37 200).

P2: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 0.71 (s, 6H), 1.01 (s, 22H), 2.01 (s, 4H), 2.86 (s, 2H), 3.51 (s, 4H), 6.61−7.73 (m, 26H). ^{13}C NMR (63 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 14.2, 23.0, 24.3, 29.6, 30.4, 32.2, 40.8, 43.0, 59.6, 112.3, 118.2, 120.5, 121.8, 126.2, 128.1, 128.6, 129.2, 129.9, 130.8, 131.4, 132.0, 133.0, 133.9, 139.2, 139.9, 140.6, 143.7, 150.0, 152.3. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 272 (20 700), 360 (67 000), 467 (20 500).

P3: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 0.94−1.65 (22H, m, b), 2.82 (4H, s), 3.60 (6H, s), 7.19−8.01 (20H, m). ^{13}C NMR (63 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 13.5, 22.5, 23.9, 27.6, 29.4, 30.9, 31.4, 40.8, 110.1, 113.0, 116.6, 116.9, 118.6, 127.3, 128.1, 128.5, 129.3, 130.0, 132.4, 135.8, 136.9, 137.9, 138.3, 139.5, 140.2, 143.4, 143.8, 146.1, 146.7, 160.1, 160.3, 160.9, 161.4. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 267 (38 900), 289 (31 200), 534 (43 500).

P4: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 0.97 (6H, s), 1.47 (4H, s), 1.76 (4H, s), 3.58 (6H, s), 4.10 (4H, s), 7.16−7.99 (22H, m). ^{13}C NMR (63 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 13.8, 19.5, 31.6, 42.4, 71.2, 117.7, 118.0, 127.6, 128.5, 129.6, 130.4, 130.8, 132.8, 136.2, 136.3, 137.3, 138.0, 138.5, 138.6, 139.3, 139.9, 143.8, 144.1, 146.4, 147.2, 150.6, 176.6. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 290 (46 200), 343 (41 500), 538 (52 500).

M1: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 3.41 (s, 6H, N−*Me$_2$*), 6.97−7.83 (22H, m). ^{13}C NMR (63 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 41.8 (N−*Me$_2$*), 107.5 (center-*C*), 127.1, 127.3, 128.6, 128.7, 129.2, 131.4, 135.8, 137.6, 138.7, 143.7, 147.6, 179.0. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 246 (24 600), 434 (25 900), 527 (44 500).

M2: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 0.67 (10H, m), 0.98 (20H, s(b)), 2.04 (4H, m), 3.43 (12H, s), 6.77−7.86 (28H, m). ^{13}C NMR (63 MHz, CD$_2$Cl$_2$/CF$_3$COOD, δ): 13.1, 21.8, 23.1, 28.4, 29.1, 31.1, 39.5, 41.3, 55.0, 120.2, 121.0, 126.0, 126.7, 128.2, 129.3, 133.4, 134.2, 135.2, 137.1, 137.6, 138.3, 140.9, 143.1, 143.2, 146.6, 151.8, 178.1. UV−vis λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): 267 (32 300), 328 (52 800), 561 (102 000).

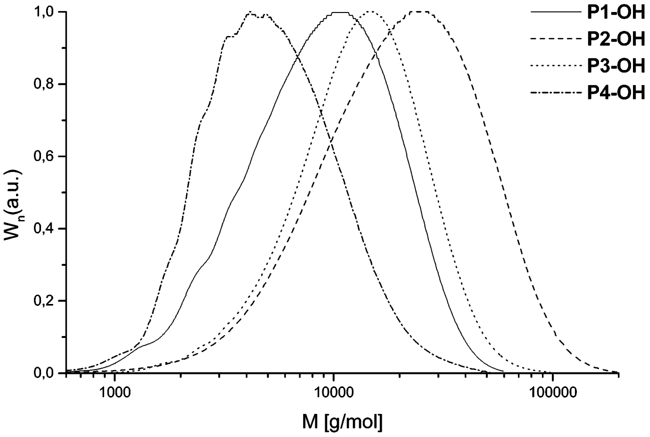


Figure 1. Normalized GPC curves of Polymers **P1-OH**−**P4-OH** in THF (polystyrene standard).

Results and Discussion

The route to the triphenylmethane carbinols used as monomers is shown in Scheme 1. The dibromofunctionalized benzophenone is achievable through the particular substituted benzoic acid chloride and a subsequent Friedel−Crafts acylation. After recrystallization from hexane, the pure products were obtained in yields of 50−70%.

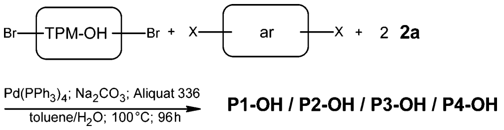
In a second step, the ketones were converted to the carbinols by reacting them in a Grignard-like reaction with 4-lithium-*N*,*N*-dimethylaniline in dry THF at room temperature. The lithium agent was preliminarily formed by dropwise addition of a THF solution of 4-bromo-*N*,*N*-dimethylaniline into a solution of *n*-butyllithium in THF.

The products were purified by column chromatography to get coarse white crystals in different yields.

The considerable differences in yields of the different carbinols are mainly due to the sterically hindered attack of the lithium agent on the 2,5-dibromobenzophenone.

The new statistical polyarylene−triphenylmethyl−carbinol copolymers **P1-OH**−**P4-OH** were prepared by standard Suzuki reaction of the dibromoarenes **1** and **3** with the diboronic monomer **2a** in equimolar ratio to both in the presence of **Pd(PPh$_3$)$_4$** and an aqueous solution of sodium carbonate and Aliquat 336 (Scheme 2). Due to the statistical reaction, the exact configuration of the polymer string, especially the amounts of *m* and *n*, were not in detail assignable. After precipitating from methanol, hexane, and diethyl ether, respectively, the polymers **P1-OH**−**P4-OH** were obtained in 44−90% yield (see Table 1).

Scheme 2. Pathway to the Aimed Polymers



Molecular weights of the polymers were determined by gel permeation chromatography (polystyrene standard/THF). The normalized curves (Figure 1) show monomodal and narrow distributions. It is remarkable that the Suzuki polycondensation with the 9,9′-dioctyl-2,7-dibromofluorene comonomer leads to higher DP values compared to the polymers **P3-OH** and **P4-OH**. With the shortening of the side chains of the comonomers, the solubility decreases. This leads to lower yields of soluble polymer and a decrease in molecular weights. After repeated precipitation, products, soluble in common solvents such as THF, chloroform, dichlormethane, or toluene, are achieved. An

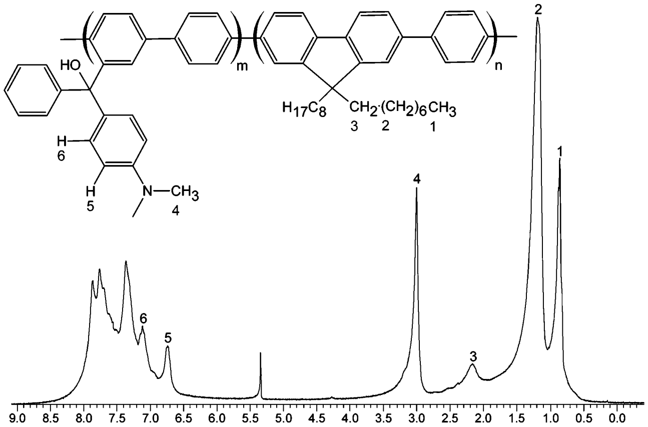


Figure 2. ^{1}H NMR of **P2-OH** (250 MHz; CD_2Cl_2).

overview of the synthesized polymers and the low molecular weight model like substances **M1-OH** and **M2-OH** is given in Table 2.

Table 2. Structural Data of the Designed Polymers

polymer	M_w [g/mol]	M_n [g/mol]	D	DP (M_n)
P1-OH	11 200	7000	1.75	8
P2-OH	26 600	13 500	2.02	16
P3-OH	15 900	10 000	1.57	14
P4-OH	6500	4000	1.7	6

The polymers were further characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, and UV−vis spectroscopy. By way of example, the ^{1}H NMR of **P2-OH** is depicted in Figure 2. The spectrum shows all expected signals, the three broad and strong signals at $\delta = 0.9$, 1.3, and 2.2 ppm for the alkyl chains located at the fluorene and a sharp singulet at 3.0 ppm for the methyl groups at the nitrogene atom. By the NMR spectra of the model substances (see Experimental Section), it could be proved that nearby this signal lies an additional signal for the OH proton, being responsible for the broad base of the signal. Due to the polymeric peak broadening, the aromatic signals are not separable from each other but show the expected intensity compared to the alkyl signals. There is no statement possible about the primary configuration of the polymers. All polymers have a statistical composition with differing lengths of phenyl−aryl and phenyl−triarylmethanoyl blocks.

The polymers were found to be thermostable up to 260 °C and showed no endo- or exotherm transition up to that temperature.

To facilitate the assignment of NMR signals and for comparison of the photophysical data of the polymers, low molecular weight compounds **M1-OH** and **M2-OH** were synthesized. The procedure is similar to that of the polymers but with shorter reactions times of 12 h. The products are purified by column chromatography in hexane/ethyl acetate 5:1 and recrystallization from the same solvent. So the NMR signals could be assigned as shown in Figure 2.

The absorption spectra of the four copolymers and the two model like substances in the carbinol forms are displayed in Figure 3.

For the fluorene containing polymers, the strong absorption around 355 nm can be seen. An expected, bathochromic shift (~20 nm) of polymers **P1-OH** and **P2-OH** compared to **M2-OH** ($\lambda_{max} = 333$ nm) is obvious. **M2-OH** also shows a greater extinction due to a greater transition moment, resulting from the higher symmetry compared to the polymers.

P4-OH shows a strong absorption at 290 nm caused by the dialkoxyphenyl group. In the spectrum of **P3-OH**, an absorption band at 302 nm is caused by a dihexylthiophene group. For a complete overview over photophysical data, see Table 1.

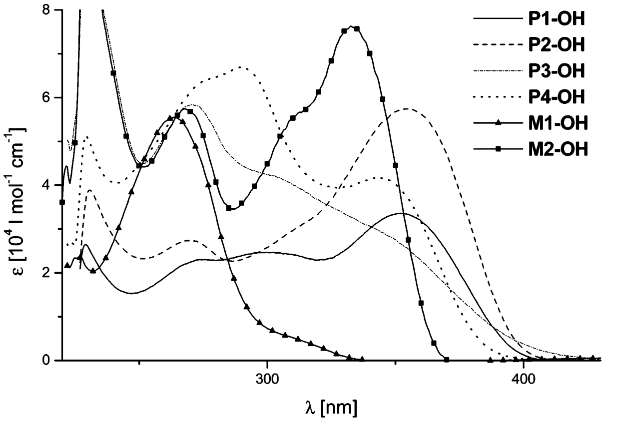


Figure 3. UV−vis spectra of polymers **P1-OH**−**P4-OH** and models **M1-OH** and **M2-OH**.

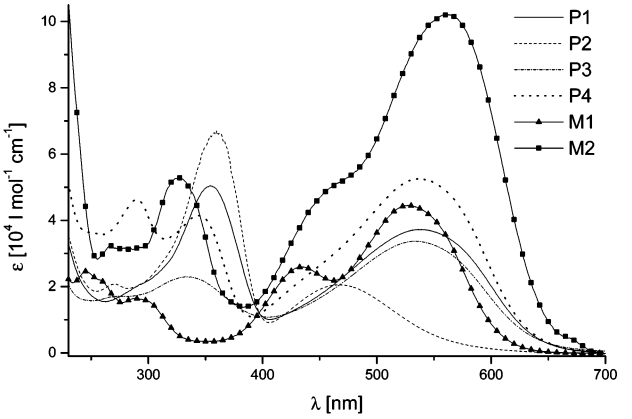


Figure 4. UV−vis spectra of polymers **P1**−**P4** and models **M1** and **M2**.

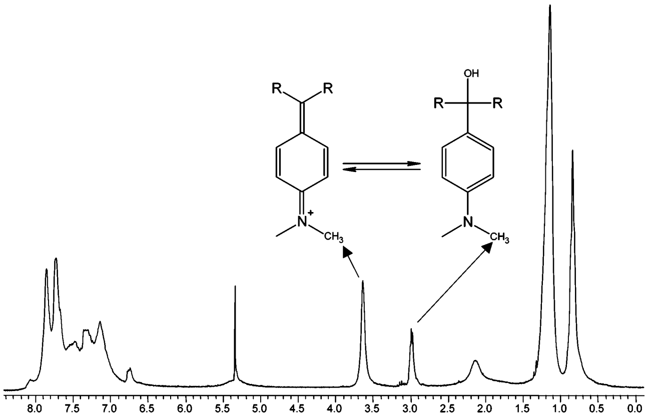


Figure 5. ^{1}H NMR (250 MHz; CD_2Cl_2/CF_3COOD) of **P2**.

To convert the triarylmethane carbinols to the colored form, the particular polymer or model substance was dissolved in dichloromethane and trifluoroacetic acid (TFA) in about 6-fold excess was added (Scheme 3). Within a few minutes, the formerly colorless solution turns deep violet. An analogous method was used by Meier et al. for triarylmethane dyes as centers of star-shaped conjugated oligomers.[18]

Consequently, the illustrated UV−vis spectra (Figure 4) reveal new strong and long-wave absorption bands around about 530 nm (see Table 3) and the nearly complete disappearance of the aniline-based absorption at 270 nm. In all polymers (**P1**−**P4**),

Scheme 3. Conversion of P1-OH to P1

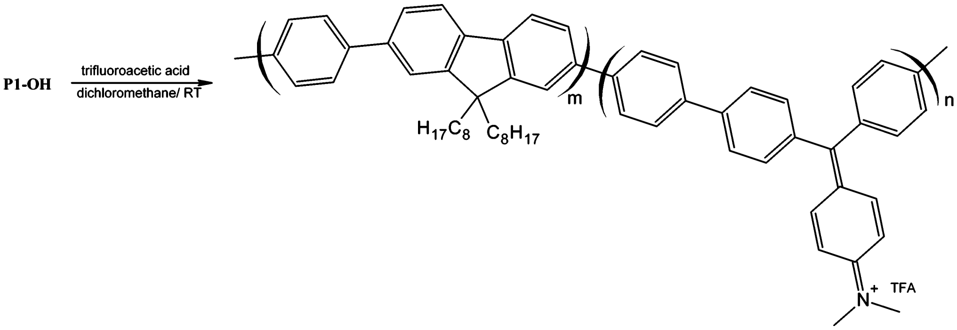


Table 3. Photophysical Data of the Polymers and Model Substances in the Colored Form

polymer/ model	λ_{max} [nm] (ϵ [L mol^{-1} cm^{-1}])	λ_{max} [nm] (ϵ [L mol^{-1} cm^{-1}])	λ_{max} [nm] (ϵ [L mol^{-1} cm^{-1}])
P1	354 (50 500)	537 (37 200)	
P2	272 (20 700)	360 (67 000)	467 (20 500)
P3	267 (38 900)	269 (31 200)	534 (43 500)
P4	290 (46 200)	343 (41 500)	538 (52 500)
M1	246 (24 600)	434 (25 900)	527 (44 500)
M2	267 (32 300)	328 (52 800)	561 (102 000)

the absorption maximum is about 10 nm red-shifted compared to **M1**.

The UV−vis spectrum of **M2** shows a very strong absorption at 561 nm ($\epsilon = 102\,000$ L mol^{-1} cm^{-1}). It is assumed that this additional 25 nm bathochromic shift results from the absence of the phenylene group between the dye and the fluorene (compared to polymers **P1** and **P2**), which leads to a better conjugation between both. Second, the bulky "polymeric rest" located at the triarylmethane dye is contraproductive for the reach of the planar quinoidic system.

In **P2**, the situation is different. The chromophoric system is located in a side chain. This partial meta position results in a lowering of the conjugation of the quinoidic system with the entire polymer. This leads to a shorter absorption maximum at 467 nm. The immense lowering of the absorption coefficient ($\epsilon = 20\,500$ L mol^{-1} cm^{-1}) indicates that the conversion of the carbinol is not quantitative. This can be proved by the ^{1}H NMR of **P2** in dichloromethane under addition of deuterated trifluoracetic acid (Figure 5). Compared to the NMR of **P2-OH**, it can be seen that there are now two signals for the methyl groups located at the nitrogen atom. These two signals have intensities of 2H ($\delta = 2.86$ ppm) and 4H ($\delta = 3.51$ ppm). This means that about 66% of the carbinol was transformed to the long-wave-absorbing form. The ^{13}C NMR spectrum (**P2** in dichloromethane under addition of trifluoracetic acid) delivers the same results by showing two signals at $\delta = 40.8$ ($-N-(CH_3)_2$) and 43.0 ($=N^+-(CH_3)_2$) ppm (see Experimental Section). In fact, all other NMR spectra show displacements of several signals compared to the particular carbinol (see Experimental section), but no NMR show signals of carbinol and long-wave absorbing form together. Obviously, the creation of the colored form processes quantitatively if the center carbon is located in the backbone of the polymer. With regard to the case at **P2**, the increase of conjugation length is a driving force for this conversion in polymers **P1**, **P3**, and **P4**.

Conclusions

In summary, we have reported on synthesis and spectroscopic study of four novel polyarylene−triphenylmethane dye copolymers.

The Suzuki cross-coupling reaction is useful to produce polyarylenes containing triarylmethane dyes as a component of the main chain. The molecular weights, determined of the leuco forms of the copolymers are in the range of 4000 (DP = 6) and 13 500 (DP = 16) g/mol. Conversion of the leuco form to the violet-colored form is done in dichloromethane with trifluoroacetic acid.

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